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DEVELOPMENT OF NON-GLASS GLAZINGS AND SURFACE COATINGS

Summary Report

By
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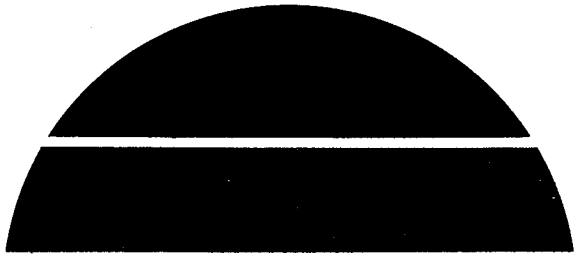
July 1981

Work Performed Under Contract No. AC04-78CS35301

Advanced Technology Laboratory
Hughes Aircraft Company
Culver City, California



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Summary Report
U.S. Department of Energy
Contract No. EM-78-C-04-5301

July 1981

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FOREWORD

This technical report was prepared by Hughes Aircraft Company, Culver City, California, under U.S. Department of Energy Contract No. EM-78-C-04-5301. The report covers work performed from 22 September 1978 to 31 December 1979.

The Hughes Principal Investigator was Dr. Norman Bilow, Senior Scientist in the Materials Technology Department. Primary contributors to the research were Dr. Richard I. Akawie, Seymour S. Schwartz, Danute I. Basiulis, Dr. Abraham L. Landis, and John R. Mosher.

Mr. Stanley W. Moore of the Los Alamos Scientific Laboratory, Los Alamos, New Mexico, served as the Department of Energy Program Monitor.

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I. INTRODUCTION

The use of glass in solar collectors suffers from several limitations, chief of which is breakage resulting from falling or thrown objects, from temperature changes, and from internal stresses. Substitution of a polymer with much higher impact resistance for glass will overcome these disadvantages. The polymer must be transparent in the wavelength range of the solar spectrum in order to allow the maximum amount of energy to pass into the solar collector. Various colorless, transparent polymers are available, but most of them do not have the capability of functioning as glazing materials at temperatures as high as 149°C (300°F). The best of these is the polycarbonate prepared from bisphenol A, made commercially by General Electric Company ("Lexan") and by Mobay Chemical Corporation ("Merlon"). These materials have good mechanical properties over a wide temperature range, particularly high impact strengths; very slight tendency to cold flow; good resistance on long-term exposure to relatively high temperatures; good dielectric properties; low water absorption; good dimensional stability; transparency in the visible and low infrared portions of the spectrum; poor long term weathering properties; good resistance to water and many organic solvents; and self-extinguishing properties. Unfortunately, the glass transition temperature (T_g) of bisphenol A polycarbonate, which is higher than its maximum service temperature, is only 149°C (300°F); its maximum service temperature is about 135°C (275°F). Therefore, it is the purpose of this program to develop polycarbonate polymers and copolymers with glass transition temperatures higher than 150°C, good optical, physical, and mechanical properties, and markedly improved resistance to ultraviolet radiation. A second objective is to develop a surface treatment that minimizes reflectance if a sufficiently good polycarbonate can be developed during the course of the program.

II. SUMMARY

Eight types of polycarbonates were synthesized, during the course of this investigation, in an effort to develop at least one which had significantly improved solar radiation stability relative to bisphenol A polycarbonate, without a serious loss of other desirable properties. Of these new materials, one was derived from a cycloaliphatic diol, two were derived from bicycloaliphatic diphenols, one was derived from a perfluoroalkylene-substituted diphenol, and three were derived from diphenols which had all of their positions ortho to the phenolic hydroxyl groups substituted by either methyl groups or chlorine atoms.

Each polymer was synthesized several times to provide products with various mean molecular weights. This was necessary to compare their relative ease of fabrication. Many of the polymers could not be processed effectively enough to yield specimens suitable for evaluation, because of either their poor melt flow characteristics, or discoloration due to degradation at their high melting points. In some cases polymer films were effectively cast from solution, even though compression molding was not satisfactory.

Thermal properties of the new polymers were studied by thermal differential analysis, thermomechanical analysis, and thermogravimetric analysis, and relative solar radiation stability was studied by exposing samples to simulated solar radiation in an Atlas Weatherometer, which also provided 9 minutes of rain per hour.

Of the various polycarbonates studied, the one derived from 4,4'-hexafluoroisopropylidenediphenol (Bisphenol AF) showed the greatest promise, since at least one sample remained unchanged through the course of the weatherometer test.

Some polymers were formulated with commercial ultraviolet stabilizers, but little benefit accrued from this approach.

III. POLYMER DEVELOPMENT

Various types of polycarbonates were synthesized during the course of this program in efforts to produce one which had improved solar radiation stability relative to bisphenol A polycarbonate, good mechanical properties, a high impact strength and a glass transition temperature over 150°C. Typical polymers which were synthesized for evaluation are listed in Table 1, and their glass transition temperatures are also shown.

Each of these polymers is described independently in the subsequent discussion, giving the reasons for selecting them for study, the various methods used for their synthesis, and the conclusions drawn from the investigation.

A. CYCLOBUTANEDIOL BASED POLYCARBONATE

Several concepts were examined to achieve the program objectives. The first of these concepts to be explored necessitated the synthesis of polycarbonates from cycloaliphatic diols such as 2, 2, 4, 4-tetramethyl-1, 3-cyclobutanediol. Such a polymer is non-aromatic, and thus it would not be capable of photochemically degrading into chromophoric quinoid compounds. Other modes of degradation can, of course, not be ruled out, but the lack of functional groups which can generate quinoid structures is certainly a big advantage.

Another reason for exploring the polycarbonate derived from 2, 2, 4, 4-tetramethyl-1, 3-cyclobutanediol was that its crystalline melting point has been reported to be 255-260°C (491-500°F)[1]. From this value, one would anticipate a glass transition temperature (Tg) in the range of 170°C, a value considerably greater than the Tg of conventional bisphenol A

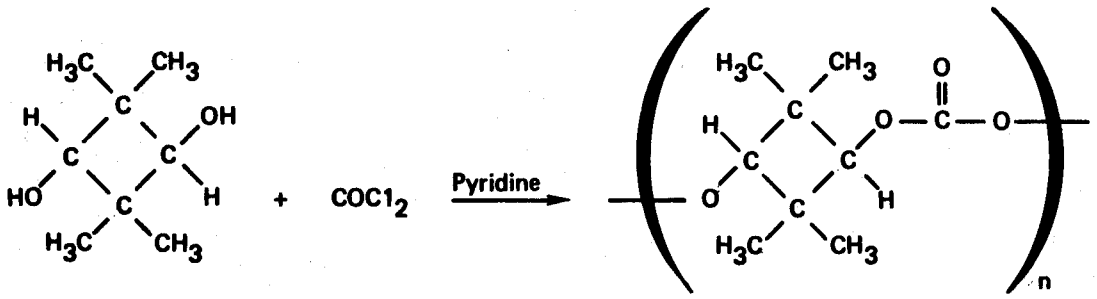
TABLE 1. POLYCARBONATES SYNTHESIZED FOR EVALUATION AND THEIR GLASS TRANSITION TEMPERATURES

Polymer Designation	Mole Ratio	T_g, °C	T_m*, °C
Tetramethylcyclobutanediol polycarbonate			380 (trans) 260 (cis)
Tetrachlorobisphenol A polycarbonate		217	260 - 275
Tetrachlorobisphenol A/ bisphenol A polycarbonate	3:7	172	
Tetrachlorobisphenol A/ bisphenol A polycarbonate	1:1	187	
Norbornylidenediphenol polycarbonate		224	
Octahydromethanoindenylidene-diphenol polycarbonate		256	
Tetramethylbisphenol A polycarbonate		205	
Bisphenol AF polycarbonate		176	
Lexan or Merlon		149	230 - 268

*T_m = melting point or range

polycarbonate (Lexan, 149°C). Therefore the former polymer would be significantly less susceptible to deformation under the high stagnation temperatures which are encountered in solar collectors.

Poly(2, 2, 4, 4-tetramethyl-1, 3-cyclobutanediyl carbonate) was prepared as illustrated below.



The synthesis procedure used was essentially that described by Union Carbide Corporation in the aforementioned patent.[1]

In this procedure, the diol, dissolved in a mixture of toluene and pyridine, was treated with a solution of phosgene in toluene. The reaction mixture was gradually heated to the reflux temperature, then cooled and filtered to remove the pyridine hydrochloride formed during the polymerization. The filtrate was then added slowly with stirring to methanol, and this caused the product to precipitate. Subsequent determination of the reduced specific viscosity gave a value of 0.17 and an inherent viscosity of 0.16 in dichloromethane at a concentration of 0.50 g/dl at 25°C.

Because its inherent viscosity was deemed inadequate, a second batch of the polymer was prepared by a slightly modified procedure. In this case the phosgene was passed into the reaction mixture as a gas, rather than dissolved in toluene. In addition, the reaction temperature was not raised above 42°C. The product was isolated as before, providing a yield of 86 percent of theoretical. This batch of polymer had a reduced specific viscosity of 0.35 and an inherent viscosity of 0.33, also taken in dichloromethane at a concentration of 0.50 g/dl at 25°C.

A third batch of this polycarbonate was prepared by an entirely different procedure. In this case 2, 2, 4, 4-tetramethyl-1, 3-cyclobutanediol was reacted with diphenyl carbonate according to a procedure described by D'Onofrio.[2]

A mixture of the diol and diphenyl carbonate, with a trace of potassium hydroxide catalyst, was heated at 210°C for 18 hours, during which time phenol, the reaction by-product, distilled from the reaction mixture. The mixture

was heated to 285-290°C for 7 hours at about 1 torr to complete the exchange reaction by removing all of the liberated phenol. The resultant product was dark and rubbery, but extraction with toluene, and precipitation with methanol gave a small yield of polymer having an inherent viscosity of 0.32 in dichloromethane at a concentration of 0.50 g/dl at 25°C. This procedure had no advantage over the previous procedure, and since it gave a poorer yield, it was not used again.

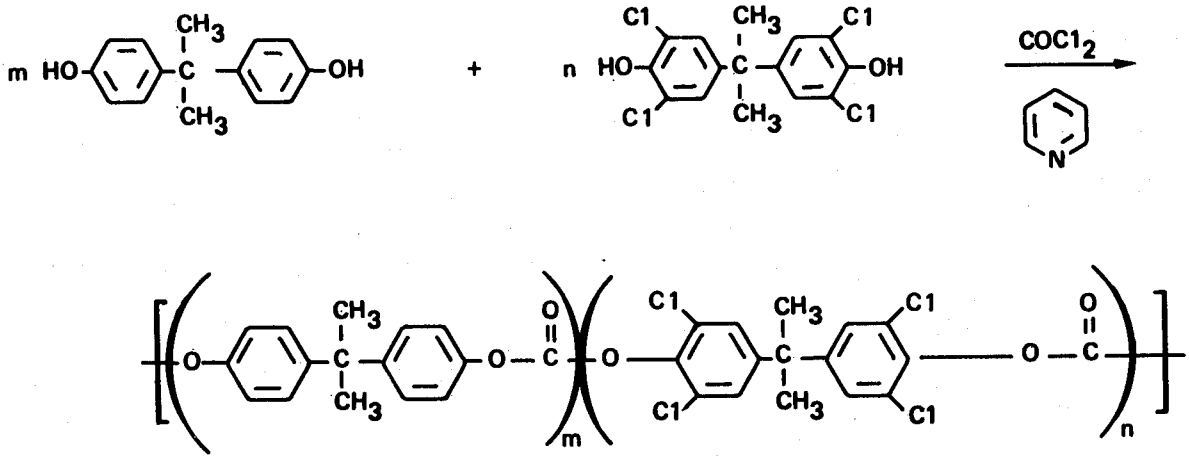
To evaluate the tetramethylcyclobutanediol based polycarbonate, 20 percent by weight solutions of the polymer in dichloromethane were prepared and efforts were made to cast films in aluminum frames onto which glass plates were bonded. The first of these polymers (IA) which had an inherent viscosity of 0.16 yielded non-coherent films containing numerous cracks. Efforts to separate the films from the glass plates were unsuccessful since the film degenerated into a powder. In part, this was due to the relatively low molecular weight of the polymer, but its crystallinity may also have been an important factor. The second batch of polymer (IB), with an inherent viscosity of 0.33, gave coherent films when cast from solution and subsequently dried. These films were, however, brittle and were not deemed suitable for further work. Films were clearest when they were about 1 mil thick, whereas thicker samples tended to be somewhat cloudy; this was another reason why their evaluation wasn't warranted. Cloudiness (blushing) was at least in part attributed to atmospheric moisture condensation, resulting from excessively rapid solvent evaporation. As a consequence, in subsequent experiments a 1:1 weight ratio toluene-xylene mixture was used to retard evaporation and prevent evaporative cooling. Such solutions provided relatively clear films, but perfect clarity still could not be obtained, even with various drying rates.

Because the solvent casting process could not be made to yield completely clear films, efforts were made to compression mold the polymer. In these experiments, the polymer in a cylindrical mold was rapidly heated to a temperature of 15-30°C above the polymer melting point, after which the mold was rapidly cooled. By constantly monitoring both temperature and pressure in the 600-1200 p.s.i. range, molding conditions were established. Although compression molded specimens were successfully fabricated, they

were not completely clear and they were excessively brittle. Thus, their evaluation was not justified and work on the tetramethylcyclobutanediol based polycarbonate was terminated.

B. TETRACHLOROBISPHENOL A BASED POLYCARBONATES

A second class of polycarbonates which were synthesized for evaluation was comprised of copolymers of bisphenol A and 3.3', 5.5'-tetrachlorobisphenol A. These materials were first prepared by the direct phosgenation of mixtures of the two bisphenols in pyridine. The polymerizations are illustrated as follows.



The basis for studying these copolymers was that tetrachlorobisphenol A polycarbonate has a very high glass transition temperature (217°C) and that the placement of chlorine atoms in all positions ortho to the phenolic OH groups was expected to inhibit photochemical rearrangement. Since the Tg of the tetrachlorobisphenol A polycarbonate is so much greater than that of bisphenol A polycarbonate (217°C vs. 147°C), it is evident that copolymers which contain both bisphenols will have intermediate Tg values depending upon their relative concentrations. Higher deformation temperatures thus can readily be built into copolymer systems. Differential thermal analysis results on one sample of homopolymer are shown in Figure 1.

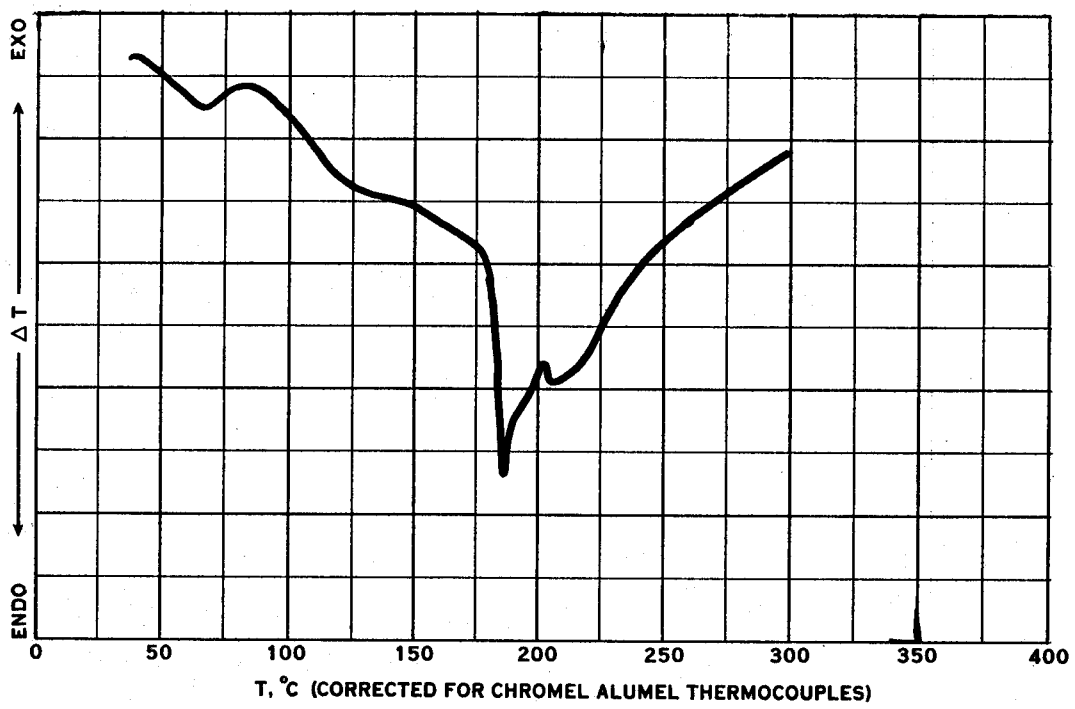
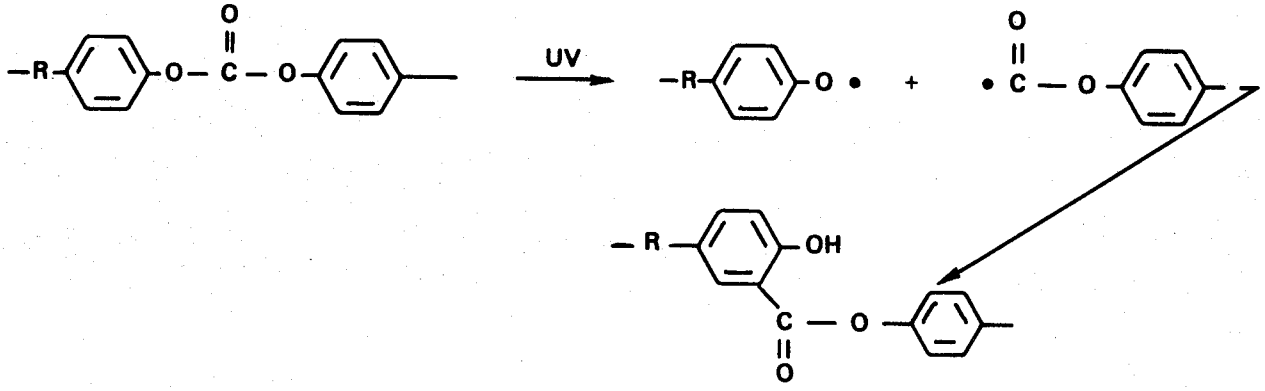


Figure 1. Differential thermal analysis of Tetrachlorobisphenol A polycarbonate.

The second reason mentioned for studying these copolymers, namely, reduced probability of photochemical degradation, is based on the fact that unsubstituted polycarbonates degrade photochemically by the following mechanism:



Once the photochemical rearrangement has occurred, the phenolic hydroxyl groups can oxidize into quinoid structures which are known chromophores. Since the rearrangements involve the ortho positions, it was thus reasoned that if the positions ortho to the phenolic group are substituted, then

rearrangement would be much less probable. For this reason, chlorine atom substitution was considered.

Tetrachlorobisphenol A polycarbonate homopolymer is, unfortunately, very brittle and so its advantages cannot be utilized in the solar collector window application. However, copolymers derived from tetrachlorobisphenol A can reasonably be expected to meet this need and therefore the tetrachlorobisphenol A research concentrated on copolymers.

Copolymers have a Tg which depends upon the weight fraction of the two individual monomers from which they are derived. The relationship is given by the equation

$$\frac{1}{Tg_{cp}} = \frac{W_1}{Tg_1} + \frac{W_2}{Tg_2}$$

where Tg_{cp} is the Tg of the copolymer, and W_1 and W_2 are the weight fractions of the bisphenols whose polymers have Tg's of Tg_1 and Tg_2. As an example, if an equimolar copolymer is prepared from bisphenol A which forms a polycarbonate whose Tg is 149°C, and tetrachlorobisphenol A, which forms a polycarbonate whose Tg is 217°C, the aforementioned equation can be used to calculate that this copolymer, containing 61 percent by weight of tetrachlorobisphenol A carbonate and 39 percent by weight of bisphenol A carbonate, would have a Tg of approximately 188°C. This is 40°C higher than that of bisphenol A polycarbonate (Lexan).

The synthesis procedure examined first was similar to that used to synthesize the polycarbonate from tetramethylcyclobutanediol. An equimolar mixture of the two diphenols, dissolved in toluene and pyridine, was treated with a solution of phosgene in toluene at a temperature gradually raised to that of reflux. The pyridine hydrochloride was filtered off, and the product was precipitated by adding the filtrate to methanol. The yield of product was 96 percent and the copolymer had a reduced specific viscosity of 0.27 and an inherent viscosity of 0.25 (in dichloromethane at a concentration of 0.50 g/dl at 25°C). A summary of inherent viscosities is presented in Table 2.

TABLE 2. SUMMARY OF INHERENT VISCOSITIES OF TETRACHLOROBISPHENOL A/BISPHENOL A COPOLYMERS

Polymer No.	Journal No.	Type of Reaction	Yield	Inherent Viscosity
1:1 Mole Ratio				
IIA	J1931-36	homogeneous reaction in pyridine-toluene	96	0.25
IIB	J1931-43	homogeneous reaction in pyridine-toluene	100	0.19
IIC	J1931-45	homogeneous reaction in pyridine-toluene	87	0.15
IID	J1931-48	homogeneous reaction in pyridine-toluene-CH_2Cl_2	59	0.35
3:7 Mole Ratio				
IIIA	J1931-52	homogeneous reaction in pyridine	78	0.17
IIIB	J1931-55	homogeneous reaction in pyridine-toluene	100	0.30
IIIC	J1931-63	interfacial reaction in H_2O/CH_2Cl_2	68	0.42
IIID	J1931-67	interfacial reaction in H_2O/CH_2Cl_2	91	0.40
IIIE	J1931-71	interfacial reaction in H_2O/CH_2Cl_2	100	0.49
IIIF	J1931-72	interfacial reaction in H_2O/CH_2Cl_2	100	0.24
IIIG	J1931-75	interfacial reaction in H_2O/CH_2Cl_2	100	0.78

A second batch of this equimolar copolymer was made by essentially the same method, except that gaseous phosgene was used in place of a solution of phosgene in toluene, and the reaction temperature was kept below 60°C. A quantitative yield of copolymer was obtained, with a reduced specific viscosity of 0.20 and an inherent viscosity of 0.19 (in dichloromethane at a concentration of 0.50 g/dl at 25°C). Because of the indicated low molecular weight of the copolymer, an attempt was made to increase the molecular weight by treating it with additional phosgene. There was some reaction, as evidenced by the formation of pyridine hydrochloride during the phosgenation, but the product of this treatment had an even lower reduced specific viscosity (0.15) and inherent viscosity (0.15) indicating that cleavage had occurred.

Another run was carried out by the process of Jackson and Caldwell.[3] In this process the two diphenols were dissolved in dichloromethane and pyridine and treated with a large excess of gaseous phosgene at ambient temperature. The workup included washing the reaction mixture with water, which resulted in an emulsion which was slow to separate. The product, obtained in 59 percent yield, had a reduced specific viscosity of 0.39 and an inherent viscosity of 0.36 (in dichloromethane at a concentration of 0.50 g/dl at 25°C).

Another batch of copolymer was prepared containing 70 mole percent of bisphenol A and 30 mole percent of tetrachlorobisphenol A. This corresponds to 60 weight percent of bisphenol A carbonate and 40 weight percent of tetrachlorobisphenol A carbonate. This copolymer should have a T_g of approximately 174°C (345°F), which is 25°C (45°F) higher than that of bisphenol A polycarbonate.

The first run was carried out using gaseous phosgene, pyridine alone as the reaction solvent, and holding the temperature near 25°C. The polymer was precipitated by pouring the reaction mixture into methanol. Next it was dissolved in toluene and reprecipitated with methanol. The yield of copolymer was 78 percent of the theoretical; it had a reduced specific viscosity of 0.18 and an inherent viscosity of 0.17 (in dichloromethane at a concentration of 0.50 g/dl at 25°C).

In the second run, phosgene was added as a solution in toluene, and pyridine and toluene were used as the reaction solvent. The workup was similar, and a nearly quantitative yield was obtained. This batch of copolymer had a reduced specific viscosity of 0.32 and an inherent viscosity of 0.30 (in dichloromethane at a concentration of 0.50 g/dl at 25°C).

The third run was an interfacial copolymerization.[4] In this case, the two diphenols were dissolved in aqueous sodium hydroxide solution, dichloromethane was present as a second phase, and phosgene dissolved in dichloromethane was added to carry out the polymerization reaction in the presence of catalysts (tertiary amine and quaternary ammonium salt). In this method, the phosgene in the organic phase reacts with the anion of the diphenol in the aqueous phase when these are mixed by stirring, and the polycarbonate which is formed goes into the organic phase. When the reaction was completed, the organic phase was separated, washed with water, and poured into methanol. The yield of copolymer was 68 percent of theoretical; it had a reduced specific viscosity of 0.47 and an inherent viscosity of 0.42.

Based on the results of this interfacial polymerization reaction, it seemed to yield a purer, less colored product with a higher molecular weight than homogeneous polymerization reactions. Also, it was found that the polycarbonates are obtained better by addition of a dichloromethane solution of the polymer, rather than a toluene solution, to methanol.

For reference and comparison, it was found that Merlon M40, which is bisphenol A polycarbonate made by Mobay Chemical Corporation, has a reduced specific viscosity of 0.58 and an inherent viscosity of 0.51.

In the course of synthesizing the tetrachlorobisphenol A copolymers by various methods, it was observed that interfacial polymerization gave the least colored products. However, since a gel had formed in the first interfacial polymerization reaction, it was thought that shortening the time of reaction would lower the molecular weight of the polymer produced and thus avoid gellation. In the second of these experiments, reaction time after addition of the phosgene solution to the diphenol phase was shortened from two hours to one hour, but some gel was still formed. The yield of copolymer

(designated IIID) was 91 percent; its reduced specific viscosity was 0.44 and its inherent viscosity 0.40.

In the next experiments, only part of the catalyst system (the quaternary ammonium salt) was present during the addition of the phosgene solution, and the other part of the catalyst system (the tertiary amine) was added when the addition was completed. In two runs in which the reaction mixtures were stirred for 60 minutes and 30 minutes, the product also gelled and had to be discarded. In two other runs, where the reaction times were 20 minutes and 15 minutes, product was successfully isolated each time in almost quantitative yield. These polymers were designated IIIE and IIIF, respectively. The inherent and specific viscosities of polymers IIIE and IIIF were measured. Polymer IIIE, prepared in a 20 minute reaction, had a reduced specific viscosity of 0.56 and an inherent viscosity of 0.49. Polymer IIIF, prepared in a 15 minute reaction, had a reduced specific viscosity of 0.26 and an inherent viscosity of 0.24. The five minute difference in reaction period thus had a profound effect upon molecular weight.

Another copolymer, containing 70 mole percent of very high purity bisphenol A and 30 mole percent of tetrachlorobisphenol A was prepared by interfacial polymerization. This batch was designated polymer IIIG. Apparently the polymerization, which was carried out for 60 minutes, proceeded to form a copolymer of higher molecular weight than before without gelling, as the solution of the product in dichloromethane was quite viscous. The copolymer was isolated as before, by precipitation in methanol, in an almost quantitative yield. It had an inherent viscosity of 0.78. It molded well, and formed discs which were slightly colored. However, transfer molding studies need to be performed on this material if optical quality specimens are to be produced.

One of the bisphenol A/tetrachlorobisphenol A copolymers (IIID) was formulated with various UV stabilizers, each in two different concentrations, namely 0.2% and 1.0%. After 62 cycles, 1488 hours (2425 solar equivalent hours) of exposure to sunshine (51 min/hr) and rain (9 min/hr), the molded disc specimens were removed from the environmental chamber and compared. Comments on their appearance are shown in Table 3.

TABLE 3. COMPOSITION OF TETRACHLOROBISPHENOL A/ BISPHENOL A COPOLYMERS CONTAINING VARIOUS UV STABILIZERS

Sample No.	UV Stabilizer*	Concentration, %	Remarks	
1	A	0.2	slight yellowing	extensive crazing
2	A	1.0	slight yellowing	extensive crazing
3	B	0.2	slight yellowing	extensive crazing
4	B	1.0	barely perceptible degradation	small amount of crazing
5	C	0.2	barely perceptible degradation	small amount of crazing
6	C	1.0	barely perceptible degradation	small amount of crazing
7	D	0.2	slight yellowing	small amount of crazing
8	D	1.0	slight yellowing	very slight crazing
9	E	0.2	slight yellowing	no crazing
10	E	1.0	pronounced yellowing	small amount of crazing
11	F	0.2	slight yellowing	small amount of crazing
12	F	1.0	pronounced yellowing	small amount of crazing
Lexan			no significant change	
Merlon			no significant change	

Copolymer IIID

*Stabilizers

A	Cyasorb 5411	D	UV Check AM-340
B	Tinuvin P	E	Adjutan 6016
C	Tinuvin 328	F	Adjutan 3516

In essentially all cases, the 0.2% concentrations were no better than the 1.0% concentrations. Furthermore, in no case did the stabilizers effectively prevent degradation. Also, it should be noted that the molding characteristics of the polymers were not good enough to yield high quality, completely transparent specimens. All specimens had slight imperfections or traces of cloudiness and thus they were not ideal samples for evaluation.

From the above study it was apparent that Tinuvin 328 was the most effective of the six stabilizers evaluated as far as color stability was concerned, even in a concentration of only 0.2%; however, only Adjutan 6016 prevented any of the crazing phenomena.

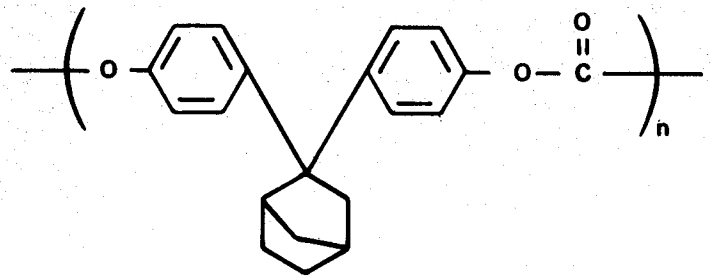
In evaluating the various stabilizers, polymer/additive blends were prepared as follows:

"Concentrated" solutions containing one gram of each stabilizer, in 20 ml. of toluene, were prepared. The polymer (48 g) then was dissolved in dichloromethane (480 ml) and the solution was divided into 24 equal parts. Diluted solutions of stabilizer (0.2% in the polymer) were made by adding 0.08 ml of the stabilizer concentrate, and concentrated solutions of stabilizer (1.0% in the polymer) were made by adding 0.40 ml of concentrate. After thorough mixing, solvent was removed by heat and vacuum. Polymers were molded under various conditions in efforts to produce optical quality specimens.

Visible spectra were measured before and after exposure to the simulated solar radiation and compared.

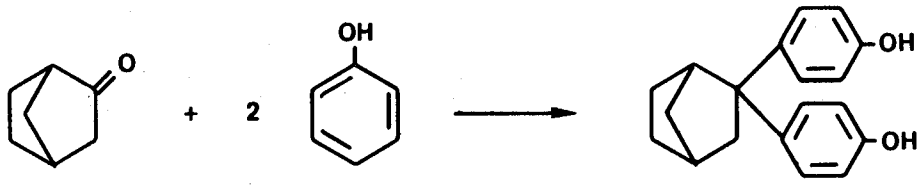
C. NORBORNYLIDENEDIPHENOL BASED POLYCARBONATES

A third type of polycarbonate studied during the course of this program was produced from 4,4'-(2-norbornylidene)diphenol. The polymer structure is shown below.



The reason for studying this material is that it has a large cycloaliphatic nucleus and consequently a lower aromatic content. In addition, its T_g is 224°C, a value which is well in excess of the T_g of conventional bisphenol A polycarbonate.

The diphenol used in the polymerization was prepared by the method of Jackson and Caldwell,[3] which is illustrated below.

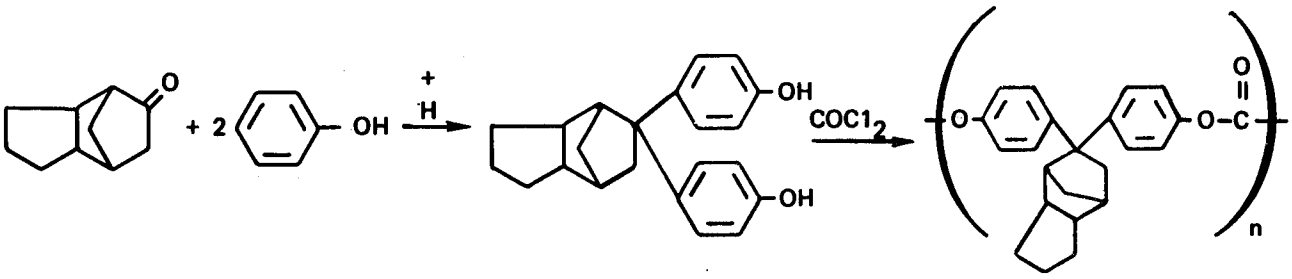


In this procedure the ketone, 2-norbornanone, was condensed with phenol in concentrated hydrochloric acid, using 3-mercaptopropionic acid as catalyst. After recrystallizing the crude product from acetic acid and xylene to remove the water of hydration, a 58 percent yield of monomer was realized. Subsequently the polycarbonate was formed by dissolving the diphenol in a mixture of dichloromethane and pyridine and then treating the mixture with a solution of phosgene in toluene. The reaction mixture was poured into a mixture of methanol and 2-propanol and the white polymer precipitated, leaving the pyridine hydrochloride salts in solution. The polymer was dissolved in toluene and precipitated with methanol, yielding a product with a grayish cast. After redissolving it in dichloromethane and precipitating it again with methanol, a white product was produced. The yield was 75 percent and the polymer had a reduced specific viscosity of 0.34 and an inherent viscosity of 0.31 in dichloromethane (0.50 g/dl at 25°C).

This diphenol was also reacted in an interfacial polymerization in aqueous sodium hydroxide and dichloromethane using tri-n-butylamine and tetraethylammonium chloride as catalysts. A stoichiometric amount of phosgene dissolved in dichloromethane was added. The reaction was quenched with glacial acetic acid after 45 minutes. After workup, a 78 percent yield of the polycarbonate was isolated. This polymer was designated VB.

Efforts to compression mold the polymer proved to be unfruitful, and clear, tough, colorless specimens could not be obtained. The very high molding temperatures which were required caused sufficient discoloration to render the samples unsuitable for optical evaluation. Samples were also quite brittle and cracked extensively when they were cooled.

A second norbornylidene-based polycarbonate also was synthesized. In this case the diphenol monomer used was 4,4'-(octahydro-4,7-methano-5H-inden-5-ylidene)diphenol. This monomer was synthesized, using the Jackson and Caldwell[3] procedure, from octahydro-4,7-methano-5H-inden-5-one, phenol, 3-mercaptopropionic acid as catalyst, and concentrated hydrochloric acid. After recrystalling the monomer from hot acetic acid, then from isopropyl alcohol, and finally from xylene, a 48 percent yield of product was realized. To form the polycarbonate, the diphenol was dissolved in a mixture of dichloromethane and pyridine and was treated with phosgene dissolved in toluene. The reaction mixture was poured into methanol, causing precipitation of the polymer and dissolution of the by-product pyridine hydrochloride salts. The polymer was isolated, washed with methanol, redissolved in toluene, reprecipitated from methanol, and dried. The yield of the product was 85 percent and the polymer had a reduced specific viscosity of 0.89 and an inherent viscosity of 0.74 in dichloromethane (at a concentration of 0.50 g/dl at 25°C). The synthesis process is illustrated below.

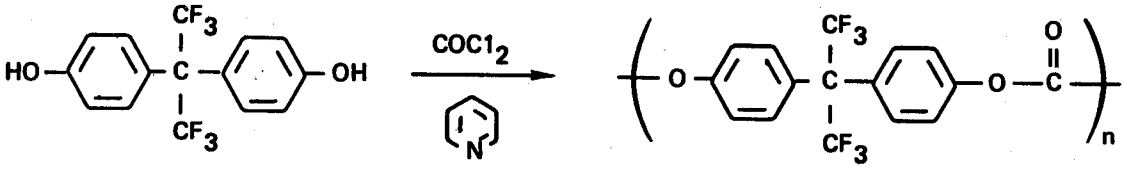


In this case also, compression molding was used to fabricate specimens but the molding characteristics of the polymer were such that high quality samples could not be realized. Discoloration was invariably observed and much crazing occurred.

Additional work on the norbornylidene-based polycarbonates thus was not carried out, since adequate evaluation did not appear to be possible.

D. BISPHENOL AF POLYCARBONATE

The fourth type of polycarbonate studied was derived from 4, 4'-(hexafluoroisopropylidene)diphenol, also known as bisphenol AF. This polymer is reported to have a glass transition temperature of 176°C,[5] although a differential scanning calorimetric analysis indicated that it could be as low as 155°C. The polymer synthesis is illustrated as follows:



Several experiments were carried out to prepare this material. In the first experiment, a solution of bisphenol AF in pyridine was treated with phosgene dissolved in toluene. Although the reaction appeared to proceed well, as evidenced by an increase in the viscosity of the reaction mixture, an attempt to precipitate the polymer by addition of methanol caused extensive hydrolysis of the product. The reaction was run again, and a mixture of acetone and methanol was used as a precipitating agent. This product had a higher molecular weight, but was still unsatisfactory. In a third experiment, a hexane-heptane mixture was used to precipitate the polymer. In this case it had an inherent viscosity of less than 0.1.

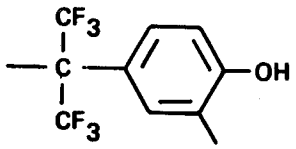
The fourth batch of polymer was isolated in high molecular weight as a pure white solid. The key factor contributing to its successful preparation was a careful purification of the bisphenol AF and the triethylamine before introducing them into the reaction mixture. The best method found for purifying the bisphenol AF was first to recrystallize the commercial product from toluene with decolorizing charcoal and subsequently to sublime the recrystallized product at 150°C using pressures of less than 1 torr. Sublimation alone is insufficient, since sublimed, but unrecrystallized, monomer still gives a polymer with some color. The triethylamine was purified by distilling a good

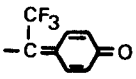
commercial grade material after treatment with phenyl isocyanate. This treatment removed primary and secondary amines which act as chain terminating agents.

The synthesis of the polycarbonate was carried out by the addition of a solution of phosgene in dichloromethane to a solution of bisphenol AF and triethylamine in dichloromethane. The product was isolated by precipitation with hexane. Precipitated polymer was freed of triethylammonium chloride by redissolving it in toluene, a solvent in which the triethylammonium chloride is insoluble, and subsequently reprecipitating it with hexane. The polymer was designated VIC. During the course of the synthetic effort it was found, by the vigorous exclusion of protonic solvents such as methanol, that the hydrolysis and the subsequent degradation of molecular weight could be prevented, even in the presence of the triethylamine-phosgene adduct. Residual amines catalyze the rapid hydrolysis, even though it has good hydrolytic stability when pure. The polymer is prepared in high molecular weight by the reaction of bisphenol AF in dichloromethane until maximum viscosity is reached. About 10 percent excess phosgene is necessary to achieve maximum viscosity.

Polymer VIC molded very well and had essentially no color. The inherent viscosity of the polymer was 0.33 (in dichloromethane, 0.5 g./dl., at 25°C). Intrinsic viscosity plots were found to be quite curved. This behavior suggests that the samples may have a wide distribution of molecular weights, or perhaps a tailing of very high molecular weight material which may need to be eliminated if brilliant clarity is to be achieved.

The reason that bisphenol AF polycarbonate was selected for study was that we believed that the hexafluoroisopropylidene group in the center of the bisphenol moiety would inhibit ring-to-ring conjugation effects even if photochemical rearrangement were to occur. Thus, in the photochemical degradation of polycarbonates, which occurs as previously illustrated on page 9, the $\rangle C(CF_3)_2$ units present in the moiety



do not allow quinoid structures such as  to form because this necessitates the elimination of CF_3 groups, a highly improbable event, considering the stability of the hexafluoroisopropylidene moiety.

As a consequence, if this chromophore does not form, then color formation would not be expected to follow.

Molding studies conducted with the bisphenol AF polycarbonate showed that it had good molding characteristics and clear specimens were successfully produced. Small defects were evident in many of the specimens, but these would not be expected if the samples were transfer molded and polymers with the optimum molecular weight for fabrication were used.

Solvent cast films of the bisphenol AF polycarbonate were also easy to prepare with either dichloromethane or toluene solutions. It was necessary to retard the evaporation to avoid blushing and provide perfectly clear films, but this was readily accomplished by partially covering the evaporating dishes with glass plates or watch glasses. Higher boiling solvents could, of course, be used to produce coatings which dried more slowly, but such formulations were not developed because this was not necessary to demonstrate that optically clear films could be achieved.

Molded specimens of polymer VIC were prepared, as were blends of VIC with 0.2 and 1.0 percent of Tinuvin P and Tinuvin 328 UV stabilizers. Specimens were placed in the Atlas Weatherometer for UV stability tests. Thirty 24 hr cycles (720 hrs, 1174 solar equivalent hours) were completed and virtually no changes were noted. Differential thermal analysis was used to determine the glass transition temperature of polymer VIC. The value was about 155°C as evidenced in Figure 2. In contrast, when analyzed by thermomechanical analysis, the Tg appears to be 143°C (see Figure 3). The polymer was also studied by thermogravimetric analysis and found to have a degradation temperature of 406°C. This result is shown in Figure 4.

A summary of the simulated solar radiation tests on bisphenol AF polycarbonate is shown in Table 4.

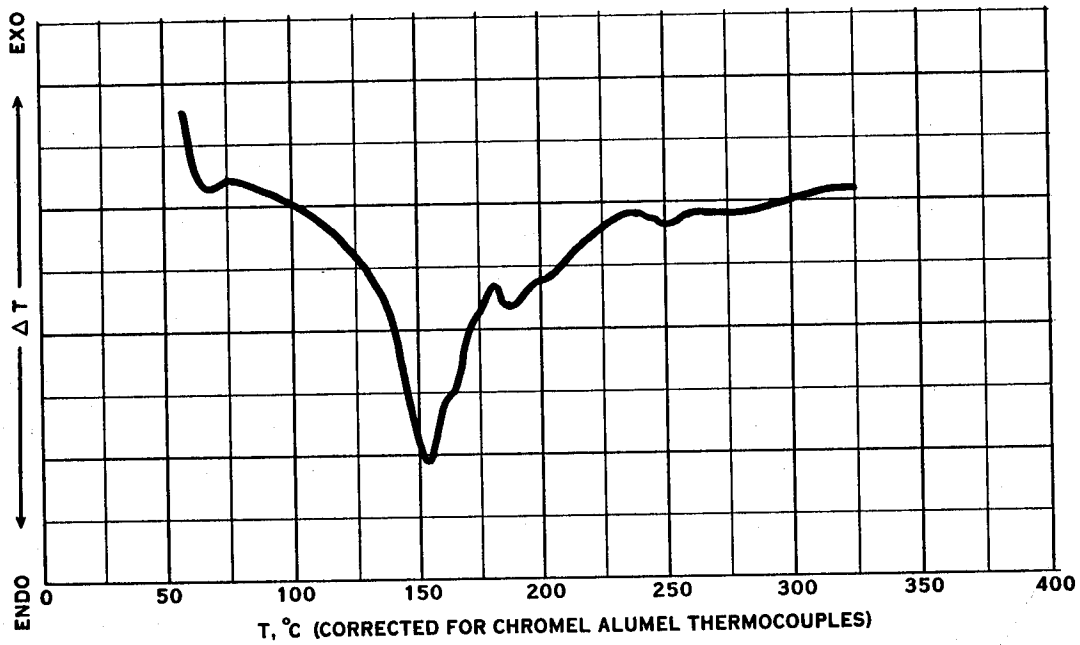


Figure 2. Differential thermal analysis of Bisphenol AF polycarbonate.

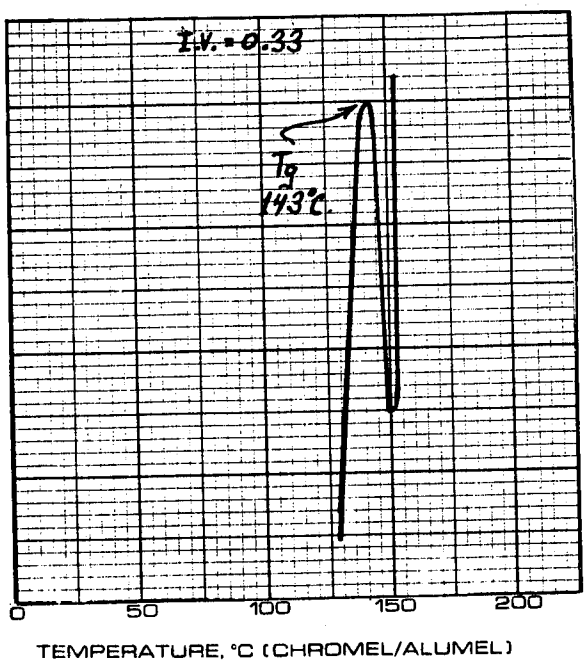


Figure 3. Thermomechanical analysis of bisphenol AF polycarbonate.

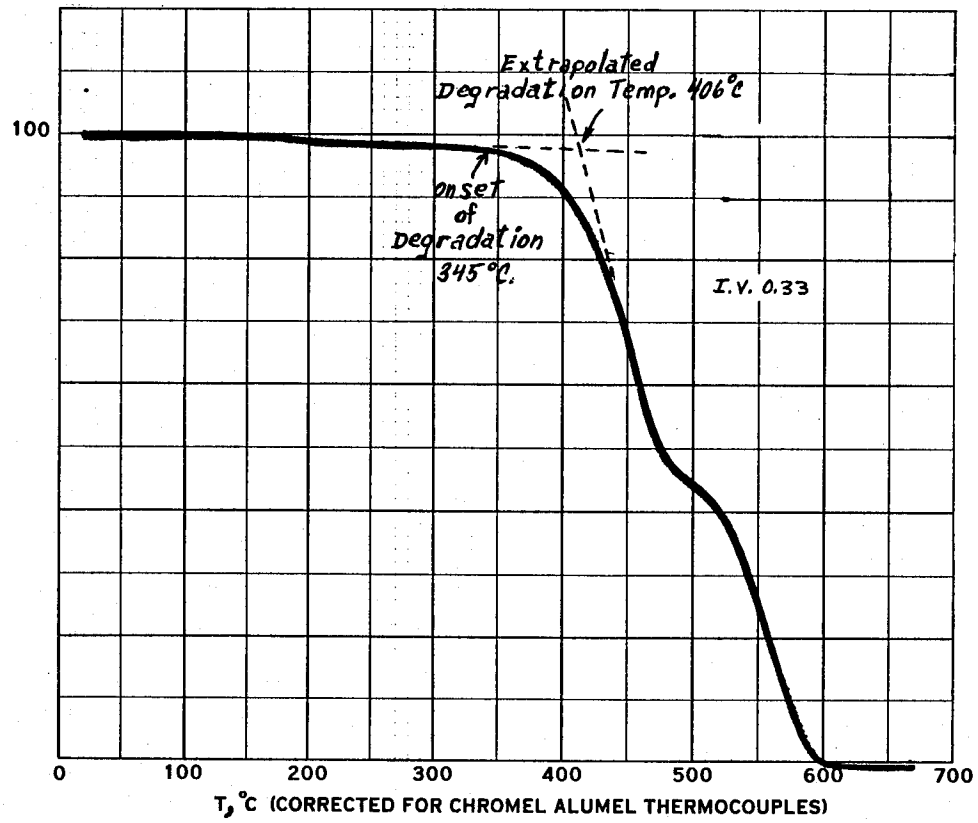


Figure 4. Thermogravimetric analysis of bisphenol AF polycarbonate.

TABLE 4. SUMMARY OF SIMULATED SOLAR RADIATION TESTS ON BISPHENOL AF POLYCARBONATE

Sample No.	Molding Temp., °C	Exposure Period, Solar Equiv. Hrs.	UV Stabilizer, %	Comments on Exposed Samples
1	260	1170	0.2% Tinuvin P	poorer than samples 5 and 6
2	260	1170	1.0% Tinuvin P	slightly less color than samples 3 and 4
3	260	1170	0.2% Tinuvin 328	essentially equivalent to 4, slightly poorer than 5 and 6
4	260	1170	1.0% Tinuvin 328	essentially equivalent to 3, slightly poorer than 5 and 6
5	220	1480	none	clarity equivalent to sample 6
6	260	1480	none	sample molded better than at 220°C

With bisphenol AF polycarbonate the stabilizer-free specimens were actually better than the stabilized specimens and the specimens which were molded at 260°F were better than those molded at 220°C. A UV/Vis absorbsion spectrum of the polymer is shown in Figure 5.

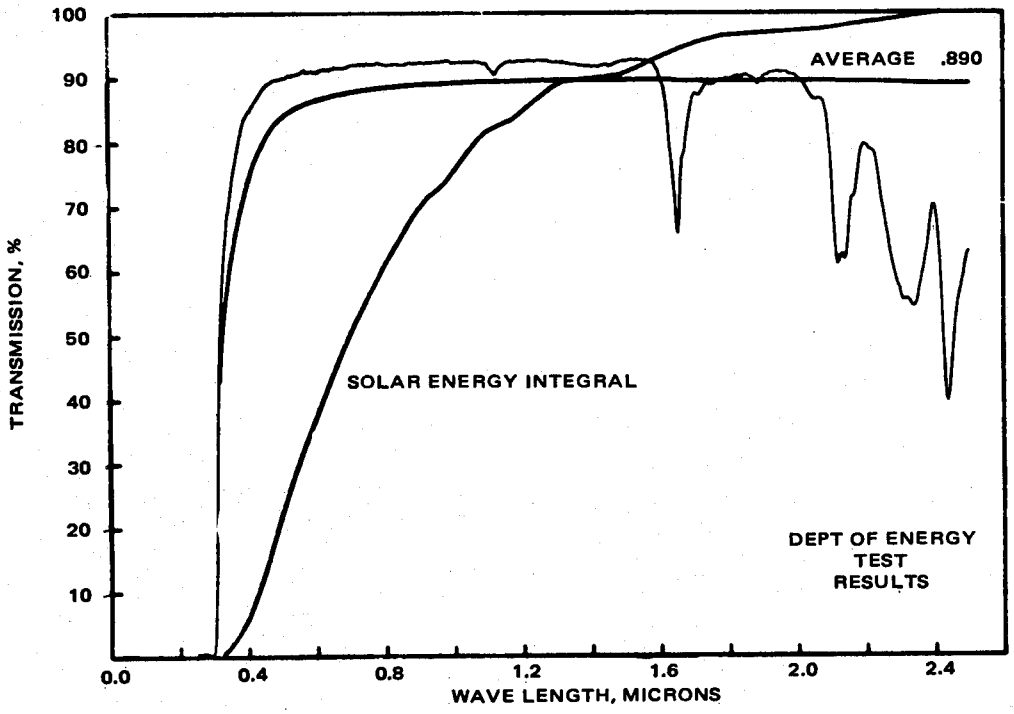
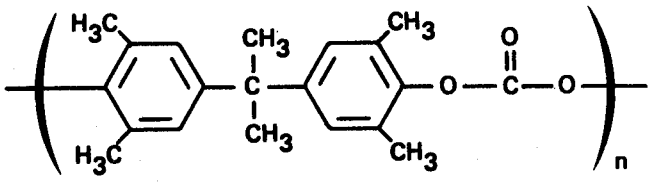


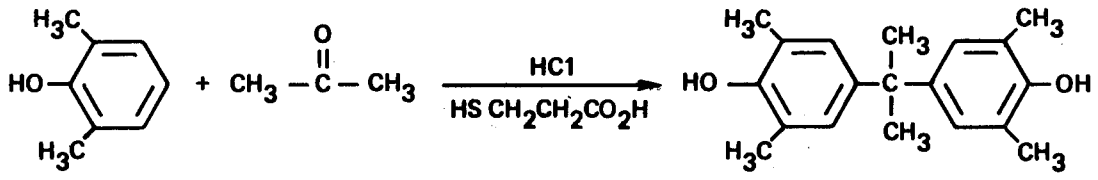
Figure 5. Bisphenol AF polycarbonate.

E. TETRAMETHYLBISPHENOL A POLYCARBONATE

A fifth type of polycarbonate studied was derived from 3, 3', 5, 5'-tetramethylbisphenol A. Its structure is illustrated below.

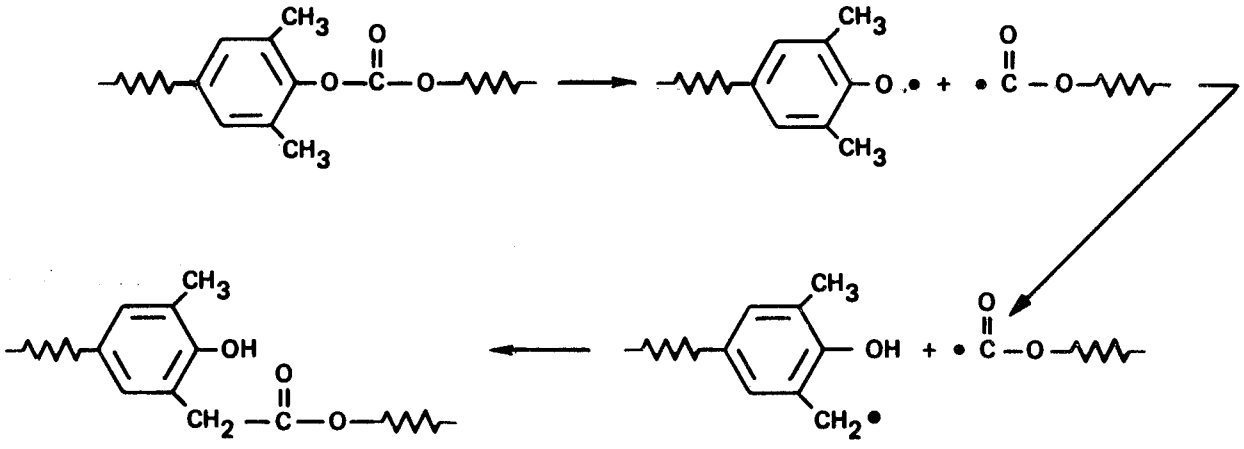


The parent monomer was synthesized from acetone and 2, 6-dimethylphenol, using 3-mercaptopropionic acid and hydrochloric acid to promote the reaction as illustrated.



White crystalline tetramethylbisphenol A was obtained in 64 percent yield.

A primary reason for selecting this polymer for study was that it has all of its positions ortho to the phenolic OH groups occupied by methyl groups. In this respect it is analogous to tetrachlorobisphenol A polycarbonate previously discussed. It was later recognized that although methyl substitution had the potential of preventing photochemically induced carbonate rearrangement as previously described, it had a potential disadvantage in that methyl groups on aromatic rings are allylic and thus are more susceptible to attack by free radicals. In this event a photochemically induced reaction such as that illustrated below may occur.



If a rearrangement such as this were to occur, photochemical degradation could not be prevented, and the reaction product illustrated would still be oxidizable into chromophoric quinoid structures.

Altogether six batches of tetramethylbisphenol A polycarbonate were synthesized. However, it should be noted that methyl substitution significantly reduces the reactivity of the hydroxyl groups due to steric hindrance and it was necessary to use a synthesis procedure which was different from that used in preparing several of the other polymers. Hence, the procedure of Serini, Vernaleken and Schnell,[6] in which the interfacial polymerization is carried out at a high pH (about 13), was used.

The first polymerization reaction was carried out by adding phosgene in dichloromethane to tetramethylbisphenol A dissolved in a sodium hydroxide solution, with tributylamine as catalyst. After several hours, more phosgene was added and the reaction was continued. The polymer was isolated by precipitation in methanol in 92 percent yield. It had a reduced specific viscosity of 0.88 and an inherent viscosity of 0.73, and was designated polymer VIIA.

Subsequently, attempts were made to shorten the reaction time for the polymerization. Polymers VIIB, VIIC, and VIID were prepared in the same way as VIIA, except that only the original amount of phosgene was used (no additional phosgene was added later) and the reaction was run for 1 hour, 3 hours, and 5-1/2 hours. The polymers were isolated as before. The 1 hour reaction time polymer (VIIC) was obtained in 92 percent yield, and had an acrid odor when heated, indicating that it contained some chloroformate end groups. The 3 hour reaction time polymer (VIIB) was obtained in 95 percent yield, and had a reduced specific viscosity of 0.40 and an inherent viscosity of 0.37. The 5-1/2 hour reaction time polymer (VIID) was obtained in 95 percent yield, and had a reduced specific viscosity of 0.48 and an inherent viscosity of 0.43. The molecular weight of the polymer evidently increased with reaction time, as would be expected.

Since the polymer with the highest molecular weight had been obtained by treating the tetramethylbisphenol A first with the customary amount of phosgene, and then with additional phosgene after several hours of reaction, another polymerization reaction was carried out using the same excess amount of phosgene, but adding it in one portion at the beginning of the reaction. The phosgene, dissolved in dichloromethane, was added to tetramethylbisphenol A dissolved in sodium hydroxide solution, with tributylamine as catalyst. The reaction mixture was stirred for 6 hours

and then the polymer was isolated by precipitation in methanol in 89 percent yield. It had a reduced specific viscosity of 0.48 and an inherent viscosity of 0.43, and was designated polymer VIIE. It had the same viscosity values as polymer VIID, which was prepared with the customary amount of phosgene in a 5-1/2 hour reaction, and lower viscosity values than polymer VIIA.

Polymers VIIB, VIIC, VIID, and VIIE were then combined and treated with more phosgene in an effort to increase the mean molecular weight. The phosgenation reaction was carried out in the usual manner with overnight stirring. The product was isolated by precipitation in methanol, and was designated as polymer VIIF. It had a reduced specific viscosity of 0.52 and an inherent viscosity of 0.46, so the molecular weight of the resultant polymer was higher than those of the starting polymers, but still not as high as that of polymer VIIA. A summary of the various experiments is presented in Table 5.

TABLE 5. SUMMARY OF YIELDS AND INHERENT VISCOSITIES OF TETRAMETHYLBISPHENOL A POLYCARBONATES

Polymer No.	Journal No.	Type of Reaction	Yield %	Inherent Viscosity
VII A	J1931-77	Interfacial reaction in H_2O/CH_2Cl_2	92	0.73
VII B	-79	Interfacial reaction in H_2O/CH_2Cl_2	95	0.37
VII C	-81	Interfacial reaction in H_2O/CH_2Cl_2	92	—
VII D	-82	Interfacial reaction in H_2O/CH_2Cl_2	95	0.43
VII E	-83	Interfacial reaction in H_2O/CH_2Cl_2	89	0.43
VII F	-85	Interfacial reaction in H_2O/CH_2Cl_2	95	0.46

The results of molding experiments on the above polymers paralleled the viscosity measurements. Polymer VIIC melted to a greenish liquid with an acrid odor, and would not form a consolidated molded disc. Polymers VIIB and VIID also did not mold well, as the discs formed were very brittle due to their low molecular weights, and crumbled in the mold. However, polymer VIIA molded very well and formed a good strong optically clear disc. It was very slightly yellow and contained some particles in it, since the polymer had not been purified extensively. Therefore, some of polymer VIIA was redissolved in dichloromethane, the solution was filtered through hardened filter paper and the polymer, designated VIIA2, was reprecipitated in methanol. This treatment removed the particulate matter but did not reduce the amount of color generated when the polymer was molded.

When polymer VIIF was molded, again good, strong, very slightly yellow, clear discs with a trace of particulate matter were obtained. Purification by column chromatography was carried out. A solution of VIIF in dichloromethane was chromatographed through neutral alumina, leaving a yellow ring at the top of the column, and then through silica gel, again leaving a yellowish band at the top of this column. The polymer was recovered by precipitation in methanol. This polymer, designated VIIF2, was molded and formed clear discs which were still slightly yellow, a little less yellow than polymer VIIF, but still not perfectly colorless. It is obvious, nevertheless, that the polymer is inherently colorless.

In a continuing effort to produce completely colorless 3,3',5,5'-tetramethylbisphenol A polycarbonate moldings, a new attempt was made to mold this polymer with an antioxidant. In these experiments, polymer VIIF2 was combined with one percent of its weight of the antioxidant, 4,4'-methylenebis(6-tert-butyl-o-cresol). However, when this mixture was molded, there was no improvement in the color of the discs produced.

The glass transition temperature of polymer VIIA was measured by differential thermoanalysis and found to be 168 $\pm 5^{\circ}$C, as shown in Figure 5. In contrast, when analyzed by thermomechanical analysis, the Tg appeared to be 178°C (see Figure 6). These values, as anticipated, are greater than that of Lexan, which has a Tg of 149°C.

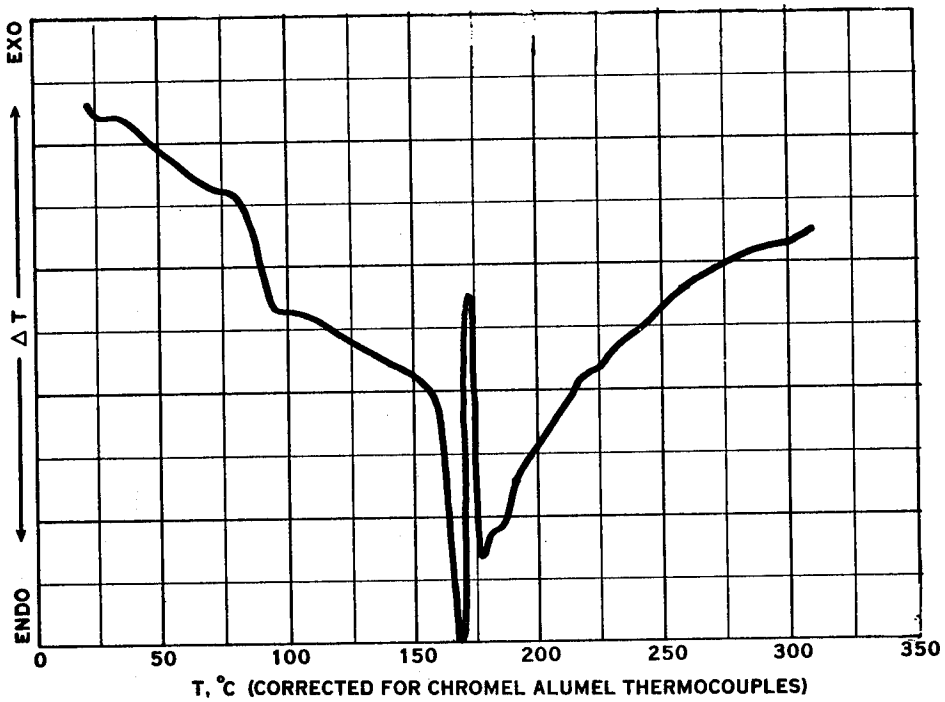


Figure 6. Differential thermal analysis of Tetramethylbisphenol A polycarbonate.

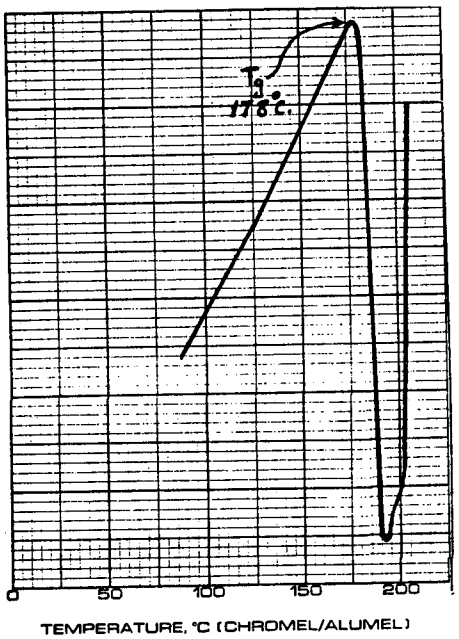


Figure 7. Thermomechanical analysis of Tetramethylbisphenol A polycarbonate.

The thermal stability of the polymer was studied by thermogravimetric analysis and the results are shown in Figure 7. A degradation temperature of 447°C was observed.

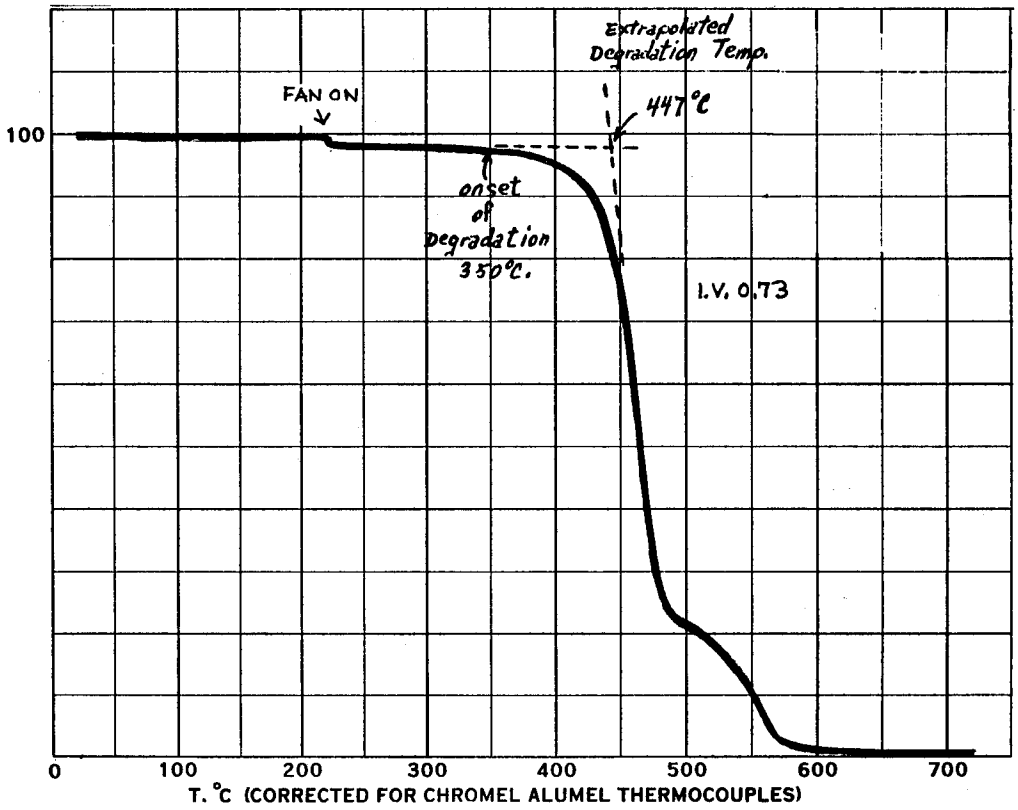


Figure 8. Thermogravimetric analysis of Tetramethylbisphenol A polycarbonate.

F. EXPERIMENTAL PROCEDURES

1. Poly(2, 2, 4, 4-tetramethyl-1, 3-cyclobutanediyl Carbonate) (J1931-40)

A 1 liter three-neck flask was fitted with a mechanical stirrer with a Teflon blade, a Dewar condenser, a thermometer, and a gas inlet tube connected to a phosgene cylinder. The condenser was connected through a drying tube to a flask containing a concentrated ammonium hydroxide solution. In the flask were placed 36.05 g (0.250 mole) of 2, 2, 4, 4-tetramethyl-1, 3-cyclobutanediol (Polysciences, Inc.), 160 ml of pyridine, and 240 ml of toluene. After the solid dissolved with stirring, phosgene was passed into the solution. Precipitate soon formed. During 40 minutes, the temperature gradually rose from 23 to 42°C, and the reaction mixture became yellowish (from formation of the phosgene-pyridine complex), so introduction of phosgene was stopped. The mixture was stirred for two hours (still yellowish), then treated with 700 ml of methanol. The pyridine hydrochloride dissolved and the product precipitated as a taffy-like material. The liquid was decanted and the solid was left in fresh methanol. The methanol was discarded and the now hard solid was dissolved in 600 ml of warm toluene, which was then added with stirring to 2 l of methanol. The white solid was filtered off, washed well with methanol, and dried in air. The yield of 36.4 g was 86 percent of the theoretical. The relative viscosity was 1.1768 (dichloromethane, 0.50 g/dl, 25°C). Hence, the reduced specific viscosity was 0.35 and the inherent viscosity was 0.33.

2. Poly(tetrachlorobisphenol A/bisphenol A Cocarbonate) (1:1 mole ratio) (J1931-48)

The apparatus was the same as above, except that a 2 liter three-neck flask was used. In the flask were placed 45.8 g (0.125 mole) of 4, 4'-isopropylidenebis(2, 6-dichlorophenol) (Aldrich) 28.5 g (0.125 mole) of 4, 4'-isopropylidenediphenol (Eastman), 125 ml of pyridine, and 750 ml of dichloromethane. The solids were dissolved by stirring. A water bath was placed about the reaction flask to keep the temperature of the solution at 25 to 30°C. Phosgene gas was passed into the solution for 3 hours. Pyridine hydrochloride precipitated in increasing amounts, and the color changed to yellowish to greenish yellow to pale green. After stirring overnight,

phosgene was passed in very slowly for 24 hours and then the mixture was left standing for 3 days. The mixture was added with stirring to water; there was much foaming, evidently from evolution of unreacted phosgene. The aqueous phase was decanted and the organic phase was washed twice with water. The organic phase became emulsified with water, and it took 2 days to complete the separation. Methanol was added to precipitate the product, which was then dissolved in warm toluene and reprecipitated with methanol twice. After drying in air, the yield of product was 59 percent of the theoretical. The relative viscosity was 1.1945 (dichloromethane, 0.50 g/dl, 25°C). Hence, the reduced specific viscosity was 0.39 and the inherent viscosity 0.36.

3. Poly(tetrachlorobisphenol A-bisphenol A Cocarbonate) (3:7 mole ratio) (J1931-75)

The apparatus used was the same as that above, except that an addition funnel replaced the gas inlet tube. In the flask were placed 40.0 g (0.175 mole) of 4,4'-isopropylidenediphenol (Aldrich, 97 percent pure), 27.5 g (0.075 mole) of 4,4'-isopropylidenebis(2,6-dichlorophenol) (Aldrich), 28.0 g (0.70 mole) of sodium hydroxide pellets, and 667 ml of water. The mixture was stirred till the solids dissolved, and was cooled to 18°C. Then were added 333 ml of dichloromethane and 1.7 g of tetraethylammonium chloride (Eastman). A cold solution of 19.1 ml (27.4 g, 0.275 mole) of phosgene in 67 ml of dichloromethane was added from the funnel with stirring over 38 minutes (the temperature of the reaction mixture was held at 18°C), and then 1.7 ml of tributylamine (Eastman) was added at once. The mixture was stirred for 60 minutes longer. The organic phase was quite viscous. The mixture was treated with 10 ml of glacial acetic acid. The aqueous phase was decanted, and the organic phase was washed twice with water. Dichloromethane was added and the solution was added with stirring to about 2 l of methanol. The solid product which formed was separated, redissolved in dichloromethane, and reprecipitated by addition to methanol. The solid was suspended in fresh methanol overnight. It was filtered off and dried in air. The yield of white product was 73.4 g, or 99 percent of the theoretical. The relative viscosity was 1.48 (dichloromethane, 0.50 g/dl, 25°C). Hence, the reduced specific viscosity was 0.96 and the inherent viscosity was 0.78.

4. 4,4'-(Octahydro-4,7-methano-5H-inden-5-ylidene)diphenol (J2332-83)

A 3 liter three-neck flask was fitted with a mechanical stirrer with a Teflon blade and a reflux condenser. The condenser was connected to an aqueous sodium hydroxide trap. In the flask were placed 103.6 g (0.69 mole) of octahydro-4,7-methano-5H-inden-5-one (Aldrich Chemical Co.), 259.6 g (2.76 moles) of phenol (Aldrich Chemical Co.), 438 ml of concentrated hydrochloric acid and 3.6 ml of 3-mercaptopropionic acid (Aldrich Chemical Co.). The reaction mixture was heated at 50°C for eight hours with stirring and then was allowed to stand for two days. The solution was filtered and the purple solids washed with water. The solids were dissolved in 1.5 l of hot acetic acid, treated with activated charcoal, and filtered with suction. The filtrate was heated to 100°C and an equal amount of hot water (90°C) was added until cloudiness was evident and persistent. Black crystals formed, which were filtered off and washed with 50 percent aqueous acetic acid and with water. The crystals were recrystallized from hot acetic acid and water, but yielded only dark product. Recrystallization from hot isopropyl alcohol yielded beige crystals, m.p. 218-219°C. These were recrystallized from hot xylene, after distilling off any water or alcohol of crystallization. A little acetone was used to help dissolve the crystals. The yield of the off-white product was 106.7 g (0.33 mole), representing a 48 percent yield. The product melted at 220-221°C (reported m.p., 221-223°C[3]).

5. Poly[4,4'-(octahydro-4,7-methano-5H-inden-5-ylidene)diphenol Carbonate] (J2332-91)

A 3 liter three-neck flask was fitted with a mechanical stirrer with a Teflon blade, a Dewar condenser connected to an oil bubbler, a thermometer, and a 150 ml dropping funnel with a gas inlet tube connected to argon. In the flask were placed 53.20 g (0.17 mole) of 4,4'-(octahydro-4,7-methano-5H-inden-5-ylidene)diphenol, 84 ml of pyridine, and 600 ml of dichloromethane. After the solid dissolved with stirring, 12 ml of phosgene dissolved in 100 ml of cold toluene (dried over molecular sieve) was added dropwise to the reaction flask. After a while precipitation of salts was

observed. The temperature of the reaction mixture did not rise above 32°C. The reaction mixture was allowed to stir for an hour and another 0.5 ml of phosgene in 20 ml toluene was added to the reaction flask. In this manner another 1.5 ml of phosgene was added. The reaction mixture was allowed to sit overnight and then was poured into 2.5 l of methanol with stirring. White polymer precipitated and the pyridine hydrochloride salts dissolved. The polymer was left to coagulate in the solution for two hours. The liquid phase was decanted and the solid phase was left in fresh methanol. The methanol was discarded and the solid was dissolved in hot toluene, treated with activated charcoal, and filtered, and the filtrate was poured with stirring into 2 l of methanol. The polymer which precipitated was washed with fresh methanol and dried in a vacuum oven at low heat. The yield of 50.0 g (0.14 mole) was 85 percent of the theoretical. The relative viscosity was 1.447 (dichloromethane, 0.50 g/dl, 25°C). Therefore, the specific viscosity was 0.89 and the inherent viscosity was 0.74.

6. 4,4'-(2-Norbornylidene)diphenol (j2332-74)

A 3 liter three-neck flask was fitted with a mechanical stirrer with a Teflon blade and a reflux condenser. The condenser was connected to an aqueous sodium hydroxide trap. In the flask were placed 100.7 g (0.91 mole) of 2-norbornanone (Aldrich Chemical Co.), 343.3 g (3.65 moles) of phenol (Aldrich Chemical Co.), 577 ml of concentrated hydrochloric acid and 4.7 ml of 3-mercaptopropionic acid (Aldrich Chemical Co.). The reaction mixture was heated to 50°C for eight hours with stirring, and was allowed to stand overnight at room temperature. The product formed round, salmon-colored pellets. The liquid was decanted through a suction filter and the product was washed with water. The solid was dissolved in 650 ml of hot acetic acid and treated with activated charcoal. After hot filtration with suction, the filtrate was heated to 100°C and 600 ml of hot water (90°C) was added. Crystals started to form. Upon cooling, more crystals formed. The crystals were filtered off and washed with 50 percent aqueous acetic acid and with water. The pink crystals were dried and recrystallized from 840 ml of hot acetic acid. After filtration, washing with 50 percent aqueous acetic acid, and then with water, white crystals, m.p. 173-174°C, were collected. The product was recrystallized from hot xylene, after distilling off any water of crystallization. A little acetone was used to help dissolve

the crystals. The yield of product was 148.7 g (0.53 mole), representing 58 percent of the theoretical. It had a m.p. of 194-195°C (reported, 199-200°C[3]).

7. Poly[4, 4'-(2-norbornylidene)diphenol Carbonate] (J2332-94)

A 3 liter three-neck flask was fitted with a mechanical stirrer with a Teflon blade, a Dewar condenser connected to an oil bubbler, a thermometer, and a 150 ml dropping funnel with a gas inlet tube connected to argon. In the flask were placed 74.00 g (0.26 mole) of 4, 4'-(2-norbornylidene)diphenol, 126 ml of pyridine, and 1 liter of dichloromethane. After the solid dissolved with stirring, 18 ml of phosgene dissolved in 125 ml of cold toluene (dried over molecular sieve) was added dropwise to the reaction flask. The temperature of the reaction did not rise higher than 33°C. After the toluene solution was almost all added, pyridine hydrochloride salt started precipitating. The reaction mixture, after addition of the phosgene was completed, was stirred for an hour, and then 4 ml of phosgene in toluene was added in increments of 1 ml of phosgene over four hours. The reaction mixture was left to sit for two days. The supernatant phase was green. The reaction mixture was poured into 2 l of a methanol – 2-propanol mixture. A white polymer precipitated. The liquid was decanted and the polymer was left to stand in fresh methanol for one day. The polymer was isolated and dissolved in hot toluene. After treatment with activated charcoal and filtration, the polymer was precipitated with methanol. The isolated polymer was grayish. Therefore, the solid was then dissolved in hot dichloromethane and reprecipitated with methanol to yield, after drying in air, 59.5 g (0.19 mole) of white polymer. The yield of product was 75 percent of the theoretical. Its relative viscosity was 1.169 (dichloromethane, 0.50 g/dl, 25°C). The reduced specific viscosity was 0.34 and the inherent viscosity 0.31.

8. Poly(bisphenol AF Carbonate) (J2324-92)

A 2 liter three-neck flask was fitted with a mechanical stirrer, an addition funnel, and a Dewar condenser with a sodium hydroxide-filled tube on the outlet. In the flask were placed 100 g (0.298 mole) of 4, 4'-hexafluoroisopropylidenediphenol (bisphenol AF, recrystallized from

toluene and sublimed under vacuum, m.p. 160.5-161.0°C), 625 ml of dichloromethane, and 90.7 g (0.898 mole) of triethylamine (distilled from phenyl isocyanate). A cold solution of 24.4 ml (34.9 g, 0.353 mole) of phosgene in 200 ml of dichloromethane was added dropwise from the funnel with stirring over a 40 minute period. Near the end of the addition, the reaction solution became very viscous and triethylammonium chloride precipitated out. The mixture was stirred for 30 minutes after the addition was completed and then was filtered. The filtrate was added to 4 l of cold hexane with rapid stirring. The precipitate was separated and dissolved in 1 l of warm toluene; the solution was cooled and filtered. The filtrate was added with stirring to 4 l of cold hexane. The white product was filtered off, dried in air overnight and then in vacuum at 150°C for 2 hours. The yield was 70 g, or 65 percent of the theoretical. The relative viscosity was 1.18 (dichloromethane, 0.50 g/dl, 25°C). Hence the reduced specific viscosity was 0.36 and the inherent viscosity was 0.33.

9. 4,4'-Isopropylidenebis(2,6-dimethylphenol) (J2749-15)

A 3 liter three-neck flask was fitted with a mechanical stirrer with a Teflon blade, a thermometer, and a condenser connected to an aqueous sodium hydroxide trap. In the flask were placed 514.3 g (4.21 moles) of 2,6-dimethylphenol (Aldrich), 61.1 g (1.05 moles) of acetone, 670 ml of concentrated hydrochloric acid and 5.5 ml of 3-mercaptopropionic acid (Aldrich). The reaction mixture was heated with an oil bath at 50°C for 5 hours with stirring, and was then allowed to cool overnight to room temperature. The reaction mixture was warmed and unreacted starting material decanted from the solid product. The solid was washed twice with water and dissolved in hot toluene; the residual water was separated. Upon cooling, solid material crystallized from the toluene. The solid was filtered off and dried to give 215.2 g of material, m.p. 161-164.5°C. The product was recrystallized from hot toluene. The yield of product was 191.0 g (0.67 mole), or 64 percent of the theoretical. It had a melting point of 165.5-167°C.

10. Poly(tetramethylbisphenol A Carbonate) (J1931-79)

A 1 liter three-neck flask was fitted with a mechanical stirrer with a Teflon blade, a Dewar condenser, a thermometer, and a 50 ml addition funnel with a gas inlet tube connected to argon. In the flask were placed 14.2 g (0.050 mole) of 4,4'-isopropylidenebis(2,6-dimethylphenol), 145 ml of dichloromethane, 190 ml of water, 1.4 ml of tributylamine, and 5.3 g (0.133 mole) of sodium hydroxide. The mixture was stirred under argon till all the solids dissolved, and was then cooled to 20°C. A cold solution of 9.0 ml (12.9 g, 0.130 mole) of phosgene in 30 ml of dichloromethane was added from the funnel with stirring over 20 minutes. The mixture was stirred for 3-1/4 hours longer, during which time 85 ml of 3N aqueous sodium hydroxide solution was added in three portions to keep the pH of the aqueous phase at 13. The two phases were separated and the organic phase was washed twice with water. The organic phase was then added dropwise with stirring to 750 ml of methanol. The product, which precipitated as very small granules, was filtered off, washed with methanol and dried under vacuum. The solid was completely melted at 265°C on a melting point block. The yield of white product was 14.8 g, or 95 percent of the theoretical. The relative viscosity was 1.20 (dichloromethane, 0.50 g/dl, 25°C). Hence, the reduced specific viscosity was 0.40 and the inherent viscosity was 0.37.

11. Poly(tetrachlorobisphenol A Carbonate) (J1931-91)

The apparatus was the same as that above. In the flask were placed 54.9 g (0.150 mole) of 4,4'-isopropylidenebis(2,6-dichlorophenol), 16.8 g (0.420 mole) of sodium hydroxide, 400 ml of water, 200 ml of dichloromethane, and 1.0 g of tetraethylammonium chloride. The mixture was milky after stirring for an hour. It was cooled to 18°C and a cold solution of 11.4 ml (16.3 g, 0.165 mole) of phosgene in 40 ml of dichloromethane was added with stirring over 32 minutes. Next was added 1.0 ml of tributylamine and the mixture was stirred for 2 hours. After addition of 6 ml of glacial acetic acid, the mixture was stirred briefly and the aqueous phase was decanted. The organic phase was washed with water, diluted with 550 ml of dichloromethane, and filtered (slow). The filtrate was added dropwise with stirring to 3 l of methanol. The product separated as a white

fibrous solid. The solid was suspended in fresh methanol overnight, after which it was filtered off, washed with methanol, and dried in air. The yield of 55.0 g was 93 percent of the theoretical.

IV. ULTRAVIOLET STABILIZATION

A. MATERIALS

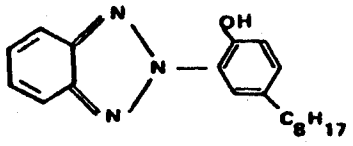
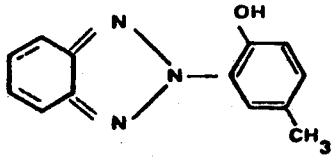
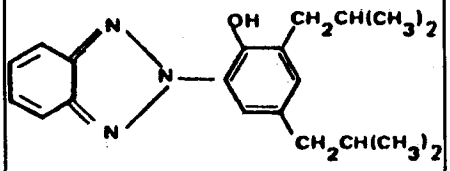
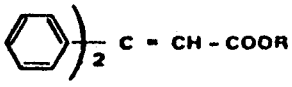
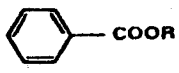
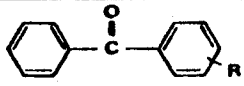
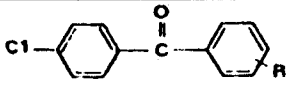
Since a major cause of degradation of polymeric materials is ultraviolet radiation emanating from the sun, it is often possible to inhibit the degradative effects of such radiation by formulating polymers with small amounts of materials which furnish protection in one or more ways. The additive may act to absorb preferentially most of the ultraviolet radiation and release the absorbed energy as heat, which is in too small an amount to be harmful. Another mechanism involves the removal of energy absorbed by the polymer before photochemical degradation of the base material takes place. Additives which act in this mode are generally called energy transfer agents. Still another protective mechanism is for the additive to decompose the organic peroxides which may be formed by the combination of ultraviolet radiation, oxygen, and the polymer base, leaving the polymer unchanged.

Among the best stabilizers for providing ultraviolet radiation protection are opaque pigments, which simply block the penetration of radiation into the polymer. Unfortunately, these cannot be used for transparent polymers. Thus, only soluble additives, generally in concentrations of from 0.2 percent to as high as 3 percent, can be incorporated into transparent polymers if the transparency is to be retained. In addition to their ultraviolet absorption or stabilization properties, the additives must not, in the concentrations used, be absorbers of visible radiation or impart a color to the host polymer.

The classes of compounds commonly found most suitable for ultraviolet stabilization of transparent materials are the hydroxybenzophenones, hydroxybenzotriazoles, acrylate esters, aryl esters, and certain organometallic compounds. From a search of the literature and vendor contracts,

it was established that various substituted hydroxybenzotriazoles were the most used materials for stabilization of polycarbonates. Consequently, several of these stabilizers were procured for evaluation. The materials obtained are shown in Table 6.

TABLE 6. ULTRAVIOLET STABILIZERS

Compound Designation	Type	Source	Chemical Name and Structure
Cyasorb 5411	benzotriazole	American Cyanamid	2-(2-hydroxy-5-tert-octylphenyl)benzotriazole 
Tinuvin P	benzotriazole	Ciba-Geigy	2-(2-hydroxy-5-methyl-phenyl)benzotriazole 
Tinuvin 328	benzotriazole	Ciba-Geigy	2-(2-hydroxy-3, 5-di-isobutylphenyl)-benzotriazole 
Uvinal N-35	diphenyl-acrylate	BASF	
AM-340	benzoate ester	Ferro Corp.	
Adjutan 6016	benzophenone	Universal Oil Products	
Adjutan 3516	p-chlorobenzo-phenone	Universal Oil Products	

In addition to procuring samples of these stabilizers, samples of polycarbonate molding pellets were obtained from both Mobay Chemical Corporation and General Electric Company. Three types of pellets were obtained: Merlon M-40, a polycarbonate without added ultraviolet absorber, Merlon M-40U, the same polymer with an unspecified benzotriazole absorber, and ultraviolet-stabilized Lexan. These materials were used as controls against which the materials developed at Hughes were compared. All three compounds are colorless, transparent pellets, which can be compression molded into colorless, transparent parts.

B. PREPARATION OF SOLVENT CAST FILMS

Samples of films were prepared by casting them from solutions of the polycarbonates plus the various stabilizers in dichloromethane or toluene. Initially, the samples were to be in the form of discs, 1 inch in diameter and approximately 1/16 inch thick. To facilitate their preparation, and avoid unnecessary handling, it was planned to cast them on small glass plates which were bonded to aluminum frames.

The polymer solutions were made initially in dichloromethane and were approximately 20 percent solids by weight. The first sample cast was made from poly(2, 2, 4, 4-tetramethyl-1, 3-cyclobutanediyl carbonate)(polymer IA), which had an inherent viscosity of 0.16. Unfortunately the resulting dried films were not coherent and exhibited considerable cracking. When attempts were made to remove the first two films from the glass plates, they tended to crumble and this was attributed to their low molecular weight. The second batch of this polycarbonate, polymer IB (inherent viscosity 0.33), had a higher molecular weight and gave coherent films on drying, but the films were excessively brittle.

These early casting experiments thus were not successful, although in several cases fair castings were obtained when very thin (approximately 0.1 mm) films were prepared. However, these films were so thin that the results of ultraviolet degradation proved to be difficult to determine. Subsequent attempts to make thicker samples resulted in cloudy films with non-uniform thicknesses.

Cloudiness in the samples was attributed to atmospheric moisture condensation (blushing), resulting from excessively rapid evaporation of solvents. Subsequently, samples were prepared using 1:1 by volume toluene-xylene mixtures. Some improvement in film clarity was noted, but perfectly clear samples were obtained only in a few cases. Varying drying speeds were tried, ranging from controlled heating on a hot plate, to open casting in air, to vacuum drying in a desiccator, to drying under a beaker on a laboratory bench. The latter procedure appeared best, since it was neither too slow nor too fast, and fair samples with less blushing were obtained. Nevertheless, except for the very thin samples, clear films were not obtained with the earliest polymers.

Subsequently, some of the polycarbonates were treated with decolorizing carbon in efforts to improve film clarity. Although the decolorizing treatments helped, they still did not always provide completely clear films.

During the latter part of the program, after methods were established for producing higher molecular weight polymers, samples were successfully solvent cast into clear films, provided that solvent evaporation was sufficiently slow. The solvent, selected after a few experiments, consisted of 55 percent dichloromethane, 40 percent toluene, and 5 percent mixed xylenes. Films of polymers were cast by dissolving the polymer in the above solvent, pouring the solution into three inch diameter petri dishes, and allowing the solvent to evaporate slowly at room temperature; watch glasses were placed over the dishes with a 1/4 inch air gap between the dish and the watch glass. Films of the polymers, each containing two percent of Tinuvin 318 (Ciba-Geigy), were also cast. The polymers formed slightly cloudy flat films.

C. COMPRESSION MOLDING STUDIES

Inasmuch as the earliest casting techniques yielded translucent samples, it was decided also to prepare compression molded disc specimens for evaluation. It was anticipated that the molding procedure would have two advantages: (1) it would eliminate the possibility of moisture-induced polymer precipitation and blushing, and (2) molding under a high pressure would coalesce the polymer particles more effectively, resulting in clearer samples.

Since only small amounts of each polymer were available, it was decided that the molded discs should be approximately 1 inch in diameter, and whatever thickness would result from 1 to 2 grams of material. The use of 1 to 2 grams of powder per sample initially precluded the use of the "Minijector," a laboratory type injection molding press which requires a minimum of approximately 10 grams of material. Although larger quantities of polymer were available later in the program, the Minijector was no longer available. Samples were therefore prepared using a fully positive compression molding die, heated and cooled in a cold platen compression molding press. To minimize polymer degradation, the cylindrical mold was quickly heated with an external heater to 10 – 25°C above the melting point of the polymer, after which the mold was rapidly cooled. The melting point was determined initially on a Fisher-Johns melting point block, and during the molding operation, by monitoring both the mold temperature and the changes in the mold pressure as the temperature was raised. The mold pressure ranged from 600 to 1200 psi, as measured with a wide scale vernier pressure gauge, and gave a better indication of the molding conditions than the temperature variations.

Using the above procedure, and sample weights of 1-1/2 grams, several colorless transparent discs, 1-1/8 inch in diameter and approximately 1/16 inch thick, were molded from the two Merlon materials. This indicated that the process would produce satisfactory samples, without visible degradation, at least in the relatively low melting control samples. Similar molding tests were made with the various batches of experimental polycarbonates. The results of these tests are given in Section III.

D. ULTRAVIOLET/VISIBLE/NEAR INFRARED ABSORPTION ANALYSIS

Absorption spectra of Lexan and several other polymers were measured over the range of 0.28 to 2.5 microns to determine if there were any absorption bands. In the Lexan spectrum, shown in Figure 8, it can be seen that minor absorptions are found at 1.13μ, 1.37μ, 1.67μ, 1.9μ and above 2.1μ. These absorptions have been interpreted as being overtones of C-H stretching vibrations and therefore they would be found in virtually all organic polymers. That they are very weak absorptions is evident from the

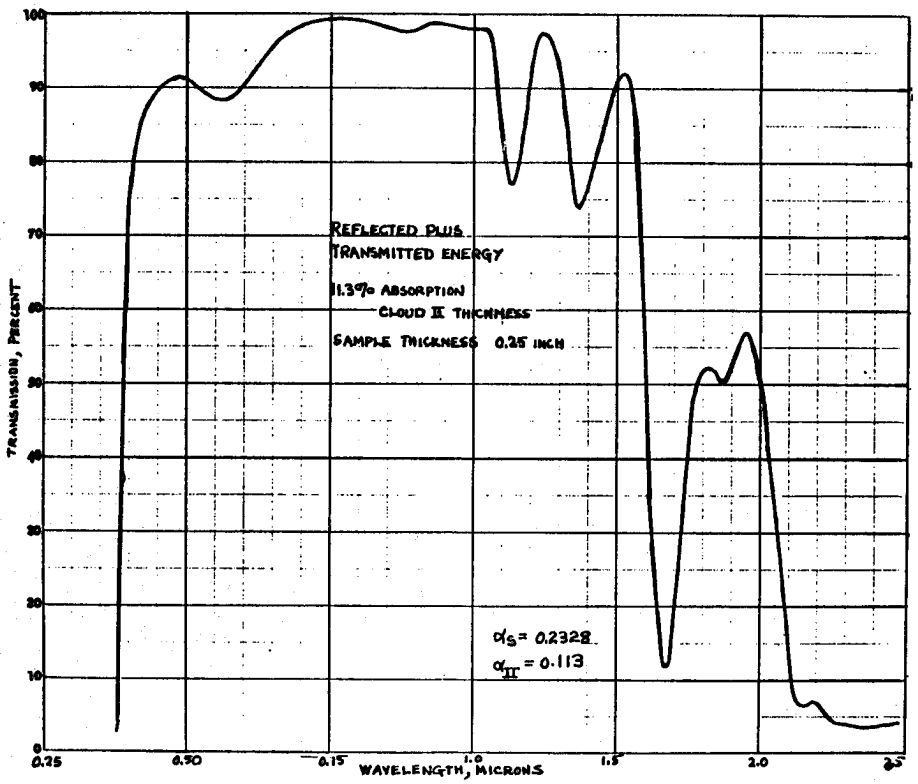


Figure 9. Ultraviolet/visible/near infrared absorption spectrum of Lexan polycarbonate.

fact that the sample tested was 1/4 inch thick and even at this thickness the weakest transmission was still above 10 percent. However, since solar radiation above 2 microns does not effectively penetrate the earth's atmosphere, the spectrum shown in Figure 8 represents an 11.3 percent near infrared absorption, assuming a cloud II thickness. Figure 10 also shows a LEXAN polycarbonate spectrum, but was prepared by DOE.

The tests show the importance of using solar collector windows having minimum thicknesses.

In the case of the films produced from the various synthesized polycarbonates, the spectra again showed slight absorption between 1.1 and 1.3 microns. There was no significant absorption up to the region of 1.6 – 1.775 microns, and then again above 2.1 microns.

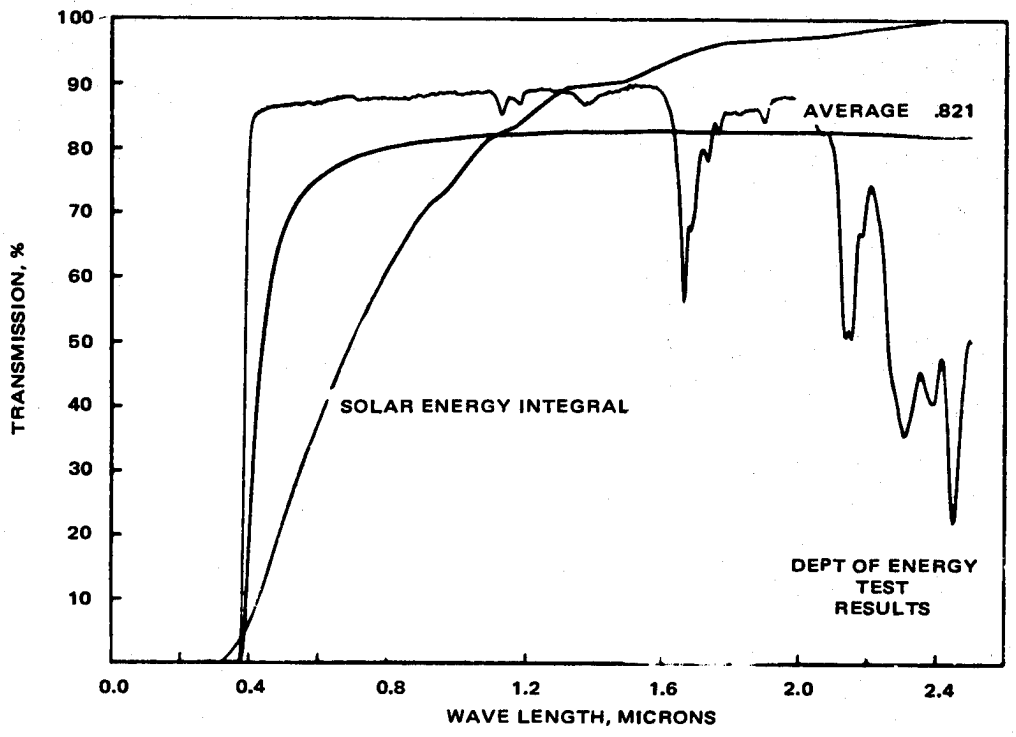


Figure 10. Milky lexan spectrum.

Visible/ultraviolet absorption spectra were also measured on a series of molded specimens after simulated solar radiation exposure, and absorption coefficients were calculated and normalized to adjust for thickness differences. Values were as follows:

Polycarbonate Type	Normalized Absorption Coefficient
Tetramethylbisphenol A	271
Tetramethylbisphenol A (reprecipitated)	158
Bisphenol AF molded at 260°C	116
Bisphenol AF with 1% Tinuvin P	84
Lexan	85

Since sample thicknesses varied, normalized absorbancy coefficients were calculated from the equation

$$C = \frac{A}{b}$$

where:

C = normalized absorption coefficient

A = absorbance = $\log \frac{1}{T}$

b = sample thickness (cm.)

T = T_A / A_C

T_A = integrated area under the transmission curve (cm^2)

A_C = integrated area corrected for transmission blank versus air

V. ANTIREFLECTION TREATMENTS

A. COATINGS

Calculations were made to determine what refractive indices and etched surface thicknesses are required to minimize reflectance losses from polycarbonate surfaces. Results of these calculations are shown in Figure 9. The calculations are based on an assumed polycarbonate substrate having a refractive index of 1.55, an etchable topcoat, and an etched surface (approximately 1 μ thick). The refractive index of the topcoat and the etched surface layer are critical and their values are as designated. For comparison, a magnesium fluoride surface coating (n = 1.38) is also shown (bottom curve). The latter gives the best results, but it will be noted that if a topcoat with a refractive index of 1.7 is applied and its surface is etched to a thickness of 1 μ and a refractive index of 1.40, then such an etched coating would be almost as good as magnesium fluoride and would transmit up to 99.5 percent of the radiant energy. Controlling an etching process to this extent would be very difficult, but not impossible. Vapor deposition of a coating such as magnesium fluoride would be much more feasible than an etching process.

Refractive index calculations were made using the equation

$$R = \left[\left(\frac{n_1 - 1}{n_1 + 1}\right) - \left(\frac{n_2 - n_1}{n_2 + n_1}\right)\right]^2 + \left(\frac{n_3 - n_2}{n_3 + n_2}\right)^2$$

This may be rewritten as a computer program in the form

$$R = [(n_1 - 1) \div (n_1 + 1) - (n_2 - n_1) \div (n_2 + n_1)]^2 + [(n_3 - n_2) \div (n_3 + n_2)]^2$$

B. SPECTRAL ABSORPTANCE STUDIES

The spectral absorptance of Lexan (General Electric Company) was measured with the Beckman DK-2A spectrophotometer. The air mass zero (AM0) solar absorptance calculated from the spectral data is $\alpha_s = 0.233$, which represents a 23 percent absorption. The absorptance of the Lexan sample was relatively large in the 1.5 μm to 2.5 μm region, and also at wavelengths shorter than 0.4 μm. Since the atmospheric absorptance is also strong in these regions,[7] a data analysis for air mass two was developed. The absorptance value for the Lexan sample for air mass two (AM2) was $\alpha_{II} = 0.113$, which represents 11 percent absorption. The AM2 value is more reasonable, and in addition, is more representative of the actual terrestrial applications. The procedure for obtaining the AM2 data (absorptances, transmittances, etc.) is more involved than the standard procedure used for AM0; however, as seen by the differences for the two values above, it is necessary.

A simple method of measuring the index of refraction of samples is needed. A method that lends itself to the sample geometries and accuracy required was investigated. This method is called the apparent depth method, and requires only a simple microscope with vernier scale. The change in focus due to the sample, together with the sample thickness, are measured. The index is then:

$$n = \frac{\text{thickness}}{\text{apparent thickness}}$$

$$\text{apparent thickness} = T_{\text{sample}} - T_{\text{focus change}}$$

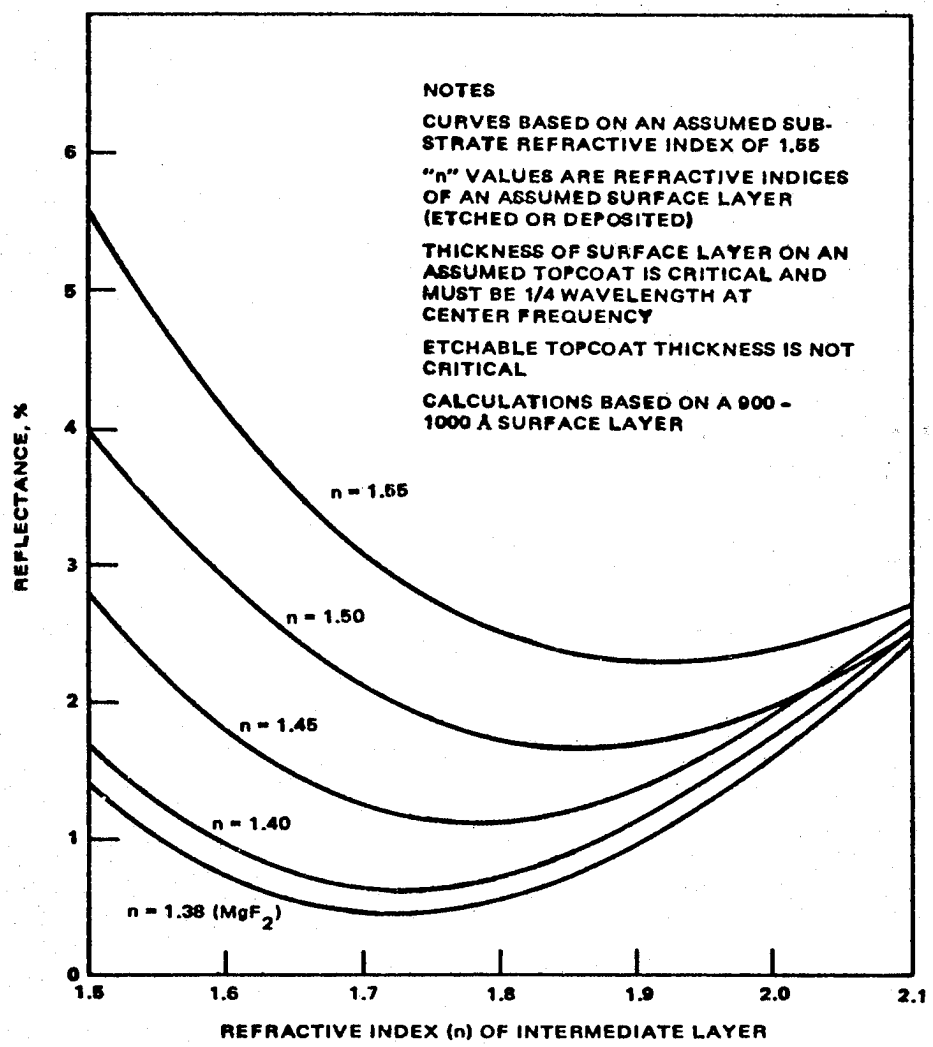
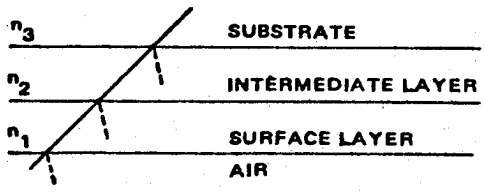


Figure11. Reflectance losses as a function of refractive index of surface layer and intermediate layer.

where R is the reflection and the refractive indices (n_1, n_2 and n_3) are as indicated below.



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